

76-1171 Mainw. G. G.

Density Separation of Small Particles by Magnetic Fluid

Sink-Float Methods A Theoretical Study

Raymond D. Mountain and J. V. Sengers
Heat Division, National Bureau of Standards
Washington, D. C. 20234

Final Report on Task 2.8

Special Analytical Techniques and Standards
(1035TCHOG/AFTAC Project Authorization No.
T/6403/NP/NBS, Amendment 3)

Introduction

This project was designed to provide a theoretical examination of phenomena associated with the separation of small particles by magnetic float sink methods. Earlier attempts to develop a magnetic fluid particle separator for small particles¹ (0.1 μm - 50 μm) have been unsuccessful for reasons that are not clearly understood. This study is intended to provide the basis for evaluating the concept itself and to serve as an aid in the evaluation of specific proposals for such devices.

From earlier work it is clear that "ferrofluids" are not suitable working fluids for magnetic separation of small particles although they are currently employed in the magnetic separation of large objects. The problems specifically associated with ferrofluids can be eliminated when a paramagnetic liquid is the working fluid. Liquid oxygen (LOX) is such a fluid and our investigation is explicitly concerned with LOX as the working fluid.

The magnetic fluid separation of particles concept is based on the following simple physical result.² If a nonmagnetic object is placed in a paramagnetic fluid subjected magnetic field gradient, the object experiences a force

$$\vec{F}_m = - \frac{1}{2} \chi_m V \text{ grad } (\vec{H} \cdot \vec{H})$$

where χ_m is the magnetic susceptibility of the fluid, V is the volume of the nonmagnetic object and \vec{H} is the applied magnetic field. By properly orienting the magnetic field, this force can be used to counteract gravitation forces and float objects which would normally sink in the fluid.

In practice, there are other physical effects operating and the object of this study is to determine how these other effects modify the float-sink concept. Specifically we consider thermal fluctuations and Brownian motion as possible causes for poor density resolution. We also examine the influence particle size and density distributions on the operation of such a device for a variety of magnetic field conditions. Finally, some observations on the physics of particle agglomeration and how to avoid it, are provided in a separate section.

Calculations for a specific magnetic field configuration, that of an approximately uniform gradient in the direction of the gravitational field, are examined in some detail. In this way a number of our conclusions are illustrated and an example of the kind of analysis needed to evaluate a specific system is provided.

It is not possible to say definitively whether or not a magnetic fluid density separator can be made to work satisfactorily with small particles (0.1 μm to 50.0 μm). The specification of a number of conditions such as density resolution required and the time available to achieve separation are needed before a specific design can be evaluated. What we do indicate is how this evaluation might be carried out. This is the main result of this study.

The effects of magnetic fields on liquid oxygen have not been studied to any extent. A bibliography prepared by the NBS Cryogenic Data Center Boulder, Colorado, contained no references directly relevant to this study and only a few of tangential interest.² Nothing was found concerning Brownian motion in LOX, with or without a magnetic field.

The examination of the magnetic float sink concept proceeds in stages. First we consider the effects associated with Brownian motion. Next, magnetic forces are included in the analysis and the possible influence of fluid fluctuations on the motion of particles is examined. The results of these investigations are used to analyze a specific example. The results of this analysis are then used to prepare a scheme for the operation of a magnetic fluid particle separator and most importantly, to pose a series of questions which must be resolved if the device is to function in a satisfactory manner.

The question of agglomeration of particles is examined in Part II of this report.

Part I

Brownian Motion

In addition to gravitational and magnetic forces, small particles in the liquid are subject to viscous forces, to Brownian motion effects and are sensitive to any mass currents in the liquid. We shall examine these effects as well as the physics associated with the tendency of small particles to agglomerate. The agglomeration of particles must be avoided if a successful particle separation device is to be developed.

A useful starting point for examining the dynamics of a particle in the liquid is the Smoluchowski equation for the probability distribution, $w(\vec{r}, t)$, of a particle subject to fluctuating forces (Brownian Motion) as well as to stationary forces.³ In this way we can compare the influence of Brownian motion effects with those of applied external forces on the motion of a particle. The equation is

$$\frac{\partial w(\vec{r}, t)}{\partial t} = D \nabla^2 w(\vec{r}, t) - \text{div} \left[\frac{\vec{K}}{\beta} w(\vec{r}, t) \right] . \quad (1)$$

Here D is the diffusion coefficient, \vec{K} is the acceleration due to external forces and β is the friction coefficient which satisfies

$$\beta = k_B T / mD. \quad (2)$$

Here $k_B T$ is the product of Boltzmann's constant and the absolute temperature and m is the mass of the particle.

An instructive example is the one dimensional sedimentation problem. There one studies the settling of a particle in a liquid due to the influence of gravity. If a particle is initially placed at a point z_0 , the probability of finding the particle at a point z at a time t later is ($z \geq 0$);

$$w(z, t, z_0) = \frac{1}{2(\pi Dt)^{\frac{1}{2}}} \left\{ e^{-\frac{(z+z_0)^2}{4Dt}} + e^{-\frac{(z-z_0)^2}{4Dt}} \right\} e^{-\frac{C}{2D}(z-z_0) - \frac{C^2 t}{4D}} \\ + \frac{C}{2D} e^{-Cz/D} \operatorname{erfc} \left[\frac{z + z_0 - Ct}{2(DT)^{\frac{1}{2}}} \right]$$

where $C = (1 - \rho_B/\rho_f) g/\beta$

is the terminal velocity of the particle if Brownian motion effects are ignored. Some numerical estimates will clarify the significance of this expression. For liquid oxygen at its boiling point⁴ ($T = 90K$),

$$\eta = 2 \times 10^{-3} \text{ P}$$

$$\rho_f = 1.14 \text{ g/cm}^3.$$

Using the Stokes-Einstein relation for a particle of radius a ,

$$D = k_B T / 6\pi a \eta, \quad (3)$$

we find

$$D = \frac{(1.38 \times 10^{-16}) (90)}{6\pi \times 2 \times 10^{-3}} \frac{1}{a} = \frac{3.29 \times 10^{-3}}{a} \text{ cm}^2/\text{sec}$$

$$C = 1.09 \times 10^5 (\rho_B - \rho_f) a^2 \text{ cm/sec}$$

For $\rho_B - \rho_f = 5 \text{ g/cm}^3$ this leads to a wide range of times required to drift 1 cm and to a range of dispersions in the expected positions. These are summarized in following table

$a(\text{cm})$	$d=2a(\mu\text{m})$	$1/C(\text{sec/cm})$	$(r^2)(\text{cm}^2)$	$(r^2)^{\frac{1}{2}}(\text{cm})$
10^{-4}	2.0	184	3.6×10^{-6}	1.9×10^{-3}
$.5 \times 10^{-4}$	1.0	735	2.9×10^{-5}	5.4×10^{-3}
$.5 \times 10^{-5}$	0.1	7.35×10^4 (2 hrs)	2.9×10^{-2}	0.17

If the numbers are inserted into $w(z, t; z_0)$ one finds very little "broadening" of the location of the particle except for particles smaller than 1 μm diameter. Even for diameters as small as 0.1 μm , the broadening is small and can be viewed as a smearing of the position predicted when only gravitational

and viscous forces are considered. This means that Brownian motion will not be a serious limitation on the magnetic fluid separation of particles unless spatial resolution of a few millimeters or less is required. From the foregoing discussion, we see that the Smoluchowski equation can be usefully employed to predict the most likely position of a small particle in a fluid. An efficient way to do this is to consider the first moment of the position variable; thus

$$\langle \vec{r} \rangle = \int dV w(\vec{r}, t; \vec{r}_0) \vec{r}$$

satisfies the equation

$$\frac{d \vec{r}}{dt} = \frac{\vec{K}}{\beta} \quad (4)$$

This is just the long time ($t \gg \beta^{-1} \approx 10^{-5}$ sec.) limit of the first integral of the mechanical equation of motion

$$\frac{d^2 \vec{r}}{dt^2} = -\beta \frac{d \vec{r}}{dt} + \vec{K}.$$

Further discussion of the motion of individual particles will be based on the solution of the equation of motion for $\langle \vec{r} \rangle$, eq (4), the expected position of the particle. The acceleration \vec{K} will be due to gravity and due to magnetic field gradients.

Before we go on to consider the magnetic force problem, it would be useful to summarize what can be learned from this example.

1. Brownian motion itself should not be a complication when forces comparable in strength to those of gravity are employed.
2. Very dense particles of micron size and greater can be moved significant distances in a few minutes, smaller and/or less dense particles will require substantially longer times.
3. The successful operation of such a device requires a very stable, motionless fluid since very low drift velocities are involved. In particular, very stable thermostating of the fluid is essential. Also this means that great care must be taken when introducing particles into the working fluid. [The procedure¹ of putting warm particles directly into liquid oxygen probably leads to mass currents of unknown spatial extent and unknown duration.]

4. It will be necessary to have complete knowledge of the acceleration field \vec{K} throughout the volume of the liquid in order to estimate the performance of any given scheme.

Magnetic Forces.

When a nonmagnetic object is immersed in a paramagnetic medium, a magnetic body force is developed if a magnetic field gradient is present. The force is

$$\vec{F}_m = - \frac{1}{2} \chi_m V \text{ grad } H^2 \quad (5)$$

where χ_m is the magnetic susceptibility of the medium, V is the volume of the object and \vec{H} is the magnetic field at the object. The effect of this body force is to expel the object from high field regions to low field regions. The force on the object depends on the volume of the particle and so the acceleration for small particles is less than it is for large ones of the same density.

The equation of motion involves the ratio of the acceleration to the friction constant,

$$\frac{\vec{K}_m}{\beta} = \frac{\vec{F}_m}{m\beta} = \frac{\frac{1}{2} \chi_m V \text{ grad } H^2}{6\pi a\eta} \quad (6)$$

For a spherical particle this becomes

$$\frac{\vec{K}_m}{\beta} = - \frac{\chi a^2 \text{ grad } H^2}{9\eta}$$

For liquid oxygen at the boiling point⁴

$$\chi = 3 \times 10^{-4} \text{ cgs units}$$

$$\eta = 2 \times 10^{-3} \text{ poise}$$

and

$$\begin{aligned}\frac{\vec{K}_m}{\beta} &= - \frac{(3 \times 10^{-4}) a^2 \text{ grad } H^2}{18 \times 10^{-3}} \\ &= - \frac{1}{60} a^2 \text{ grad } H^2 \text{ cm/sec}\end{aligned}$$

For $a = 10^{-4}$ cm in a field of 10^4 Oe and a gradient of 10^3 Oe/cm,

$$\frac{K_m}{\beta} = \frac{2 \times 10^{-8} \times 10^7}{60} = \frac{1}{300} \text{ cm/sec.}$$

This is comparable to the sedimentation velocity of a 10^{-4} cm particle of density 6 g/cm.

The magnetic term combines with the gravitational one to provide the equation of motion for a particle;

$$\frac{d\langle \vec{r} \rangle}{dt} = \hat{j}(\rho_B - \rho_f) a^2 (1.1 \times 10^5) - \frac{a^2 \text{ grad } H^2}{60}.$$

Here the gravitational field acts in the +y direction, hence the presence of \hat{j} , the unit vector in the y-direction. Magnetic flotation will occur if

$$(\rho_B - \rho_f) (1.1 \times 10^5) - \frac{|\vec{H}| \partial |\vec{H}| / \partial y}{30} < 0.$$

This requires that the field strength increase as the depth of the fluid increases. The rate with which a particle moves depends on the square of the radius so small particles will move much more slowly than do large ones. This may provide a limit on the effectiveness of magnetic separation as a way of sorting very small particles by density.

Fluctuations:

The force \vec{F}_m is the result of the magnetic stresses in the fluid. The force on a fluid element of volume V is $-\vec{F}_m$. Since the fluid undergoes density fluctuations in a volume V , the force $-\vec{F}_m$ will also undergo fluctuations of magnitude

$$\frac{\delta F}{V} = \delta M |\nabla H|$$

with

$$\delta M = \left(\frac{\partial M}{\partial n} \right)_T \delta n$$

being the variation of the magnetization with n , the number density of the fluid. The mean square fluctuations in the force are

$$\frac{(\delta F)^2}{V^2} = |\nabla H|^2 \left(\frac{\partial M}{\partial n} \right)_T^2 (\delta n)^2 / V^2$$

and

$$\frac{(\delta F)^2}{F^2} \approx \frac{(\delta n)^2}{n^2} = \frac{k_B T}{V} \kappa_T$$

when

$$\left(\frac{\partial M}{\partial n} \right)_T = \text{const.}$$

and κ_T is the isothermal compressibility of the fluid.

Using $T = 90$ K, $\kappa_T = 2 \times 10^{-4} \text{ atm}^{-1}$ and $a = 10^{-4} \text{ cm}$

$$(\delta F)^2 / F^2 = 5 \times 10^{-14}$$

or

$$(\delta F)^2 \approx 2.2 \times 10^{-7} F.$$

The fluctuating force on a fluid element is small and therefore we expect the fluctuation in the magnetic force acting on a particle also to be small. It would be possible to go through the analysis involved in taking these fluctuations into account. However, experience with non-magnetic fluctuations indicates that no significant changes in the equations are likely.⁵ For this reason, we do not concern ourselves with fluctuations in the magnetic force terms.

An Example

If one knows the forces acting on a particle, it is possible to determine the path a particle will follow by solving eq. 4 (numerically if necessary). By doing this for a variety of parameters and initial conditions it is possible to obtain a picture of how a particle device might function. This does not specifically take agglomeration into account. It does, however, provide one with the means of estimating the effects of agglomeration. This is described extensively in the appendix where it is indicated that the best way to avoid agglomeration is to avoid close encounters. Put simply, the moving particles should not collide. The solutions in turn tell us whether or not this condition is satisfied and perhaps how to avoid it.

The earlier laboratory work¹ used a magnetic field which can be approximately described as

$$\vec{H} = \Gamma(1 - \alpha z^2)^{\frac{1}{2}} \left[\hat{i} y + \hat{j} x \right].$$

The $(1 - \alpha z^2)^{\frac{1}{2}}$ factor is intended to approximately account for the fall off of the field due to the finite extent of the pole faces. As we shall see, this factor is very important and the effect must be included if any reliable analysis of particle motion is to be made. We assume $\alpha = 0.021$ based on field mapping studies of the laboratory situation in the earlier work.¹ With this magnetic field, the equation of motion (eq. 4) is a set of three coupled differential equations;

$$\frac{dx}{dt} = - \frac{\chi (a \Gamma)^2}{9\eta} x (1 - \alpha z^2)$$

$$\frac{dy}{dt} = \frac{2 g a^2}{9} (\rho_B - \rho_f) - \frac{\chi (a \Gamma)^2}{9} y (1 - \alpha z^2)$$

$$\frac{dz}{dt} = \frac{\chi (a \Gamma)^2}{9} \alpha z (x^2 + y^2).$$

We are interested in the region

$$0 \leq x \leq 2.5$$

$$3 \leq y \leq 8$$

$$0 \leq z \leq 2.5$$

as this represents the working volume of fluid available in the earlier study. This assumes $+x$ and $-x$ are equivalent as are $+z$ and $-z$. Before going further, it is necessary to know what sort of density separation is desired. We shall suppose that only particles with densities greater than 7 g/cm^3 are of interest. We use this fact to determine the field gradient parameter Γ as follows. For $x=z=0$, $y=5 \text{ cm}$, $dy/dt = 0$ for $\rho_B = 6 \text{ g/cm}^3$ when $\Gamma = 2.6 \times 10^3 \text{ Oe/cm}$. This choice for Γ should yield the desired separation if appropriate precautions are taken. The nature of these precautions can be inferred from the accompanying table which contains the solution to the equation of motion for the following conditions.

$$a = 10^{-3} \text{ cm } \Gamma = 2600 \text{ Oe/cm}$$

$$x(0) = 2.0 \text{ cm } y(0) = 5.0 \text{ cm } z(0) = 0.5 \text{ cm.}$$

$$\rho_B = 4.0 \text{ g/cm}^3, 6 \text{ g/cm}^3, 8 \text{ g/cm}^3$$

Solutions for the example

t	$\rho_B = 4 \text{ g/cm}^3$			$\rho_B = 6 \text{ g/cm}^3$			$\rho_B = 8 \text{ g/cm}^3$		
	x	y	z	x	y	z	x	y	z
0	2.00	5.00	.50	2.00	5.00	.50	2.00	5.00	.50
2	1.60	4.56	.57	1.60	4.95	.57	1.60	5.34	.58
4	1.28	4.20	.63	1.28	4.90	.65	1.28	5.70	.67
6	1.02	3.92	.68	1.02	4.87	.73	1.02	5.83	.79
8	.82	3.69	.73	.82	4.85	.82	.82	6.01	.93
10	.65	3.52	.78	.66	4.83	.92	.66	6.16	1.12
12	.52	3.37	.83	.53	4.83	1.02	.53	6.30	1.34
14	.42	3.26	.87	.42	4.83	1.15	.43	6.43	1.63
16	.34	3.17	.91	.34	4.83	1.28	.35	6.56	1.89
18	.27	3.10	.96	.27	4.84	1.43	.28	6.71	2.45
20	.17	3.04	1.00	.22	4.86	1.60	.23	6.91	3.05
22	.14	3.00	1.05	.18	4.89	1.79			
24	.11	2.97	1.09	.14	4.93	2.01			
26	.09	2.94	1.14	.12	4.98	2.25			
28	.07	2.92	1.19	.10	5.04	2.53			
30	.06	2.91	1.24						
32	.05	2.90	1.29						
34	.04	2.90	1.34						
36	.03	2.89	1.39						
38	.02	2.89	1.45						
40	.02	2.89	1.51						
42	.02	2.90	1.57						
44	.01	2.90	1.63						
46	.01	2.91	1.70						
48	.01	2.92	1.77						
50	.01	2.93	1.84						
52	.01	2.94	1.92						
54	.00	2.95	2.00						
56	.00	2.97	2.08						
58	.00	2.98	2.17						
60	.00	3.00	2.26						
62	.00	3.02	2.34						
64	.00	3.05	2.46						
66	.00	3.07	2.58						

The most striking feature is a direct result of the z -dependent terms----all particles will sink eventually if other constraints are not imposed! Thus the imposition of walls with traps is essential to enforce spatial separations once achieved. Suppose such a wall were placed at $z = 2.5$; then the 4 g/cm^3 particle would be constrained at $y=3 \text{ cm}$, the 6 g/cm^3 particle would be constrained at $y=5 \text{ cm}$ and the 8 g/cm^3 particle would settle to $y=6.7 \text{ cm}$. This would be a reasonable separation.

The factor a^2 occurs in all right hand terms of the equation of motion, so different sizes differ only in the time, τ , required to reach their destinations. τ and a are related by $\tau a^2 = \text{constant}$. The process described in the table is completed in 65 sec. for $a = 10^{-3} \text{ cm}$ particles. For $a = 5 \times 10^{-5} \text{ cm}$ particles this time is

$$\tau = \frac{(65) (10^{-6})}{25 \times 10^{-10}} = 26000 \text{ sec} \approx 7 \frac{1}{4} \text{ hrs.}$$

A constraint on the allowed initial coordinates becomes apparent upon considering the trajectory of the 6 g/cm^3 particle. Large particles of this density will be rapidly moved along their path, sweeping up the smaller diameter, more slowly moving particles as they go, unless the initial conditions are chosen so that there are no particles in the path.

The initial conditions leading to the table correspond to starting the particles out in about the middle of the volume of fluid. This seems preferable to starting them on the surface, $y(0)=3$, because the opportunities for dense, small diameter particles to be agglomerated with less dense particles by the sweeping mechanism are greater when the desired and undesired particles are moved in the same direction. Put more positively, the value of $y(0)$ and the field gradient Γ should be such that only the desired particles sink and the others are collected on the walls at or above $y=y(0)$. As noted in the appendix, surface agglomeration can be a problem so placing particles directly on the liquid surface should be avoided in any case.

We note again that the speed of the particles is very low and any velocity field in the fluid would completely override the magnetic separation, thus the need for an absolutely quiet working fluid.

Changing the x and z values of the initial conditions does not seriously alter the times required for separation to occur. However, if $z(0)$ is too large, even the dense particles will be trapped on the wall rather than reaching the "bottom". Variations in $x(0)$ are relatively insignificant as the forces tend to center the particles in the $x=0$ plane.

Conclusions

Based on the example just considered, it is possible to suggest a sequence of events and to pose a series of questions which must be satisfactorily resolved if density separation is to take place. This scheme embodies the recommendations of this report on the feasibility of developing a magnetic fluid particle separator for small particles.

1. Introduce dispersed particles into LOX in a magnetic field gradient.
 - (a) How is the initial dispersal achieved? (The theory of deagglomeration is nonexistent so empirical methods, such as sonic agitation should be considered).
 - (b) Are the particles in thermal equilibrium with the LOX?
(If they are not at the same temperature, velocity fields of unknown magnitude and duration may result. This would invalidate the analysis of the system).
 - (c) What are the allowed initial coordinates? (Initial values should lead to adequate spatial resolution).
2. The particles move according to the applied forces.
 - (a) Are there any fluid flows of thermal or mechanical origin?
(As noted above, flows in the LOX must be eliminated).
 - (b) Will a significant amount of trajectory crossing occur?
(If it does, the large diameter particles may sweep up the small diameter ones and invalidate the results.)

3. Collect the particles with the desired density separation.

(a) How important are particle-surface interactions?

(Will the particles, upon reaching a wall stick or move parallel to the wall under the action of the applied forces? This will determine what is needed to trap the particles).

(b) What sort of density resolution is required? (This is central to evaluating any design).

(c) How long is one prepared to wait for separation to occur?

(This involves both the field homogeneity in the z-direction and the stability of the LOX pool. Inhomogeneity reduces the range of acceptable initial conditions thereby extending the time required to process a given amount of material. The time interval over which the cryogenic system is stable places an upper bound on the separation time which in turn dictates such things as Γ and the initial coordinates).

The resolution of these questions may require extensive calculations of particle trajectories in order to come up with satisfactory operating conditions and satisfactory designs. Such detailed work is best done when specific designs are being examined. For this reason, no attempt has been made to evaluate the example further.

References

1. "Ferrofluid Density Separation System", Technical Reports. AFTAC PA No. VT/5415/-/ETR, Contract No. - F08606-74-C-0064.
2. A. Dupré, A. van Itterbeek and G. Brandt, Physica 28, 353 (1962).
3. S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).
4. Handbook of Chemistry and Physics, 56th edition.
5. E. H. Hauge and A. Martin-Löf, J. Stat. Phys. 7, 259 (1973).

Part II

Coagulation of particles

Introduction

In order to obtain an effective density separation mechanism for small particles it is not only sufficient that particles of different density experience a driving forcing directing them to a different level in the suspending fluid, but they also should be prevented from coagulating within the time scale of the separation process. Therefore, from a survey of the literature we have made an attempt to answer the following questions: (a) What are the factors and mechanisms leading to the coagulation of particles, (b) What are the available theoretical methods to evaluate the coagulation process, (c) and to what extent are the available methods applicable to the fluid density separator under consideration?

From the outset it should be mentioned that the time limitations of the current phase of the project only allowed us to make a cursory examination of the literature. As a result, this section of the report on the coagulation of particles must necessarily be a preliminary one. Basically we present a number of remarks on what one can and what one cannot expect from a theoretical treatment of the coagulation process for the problem at hand.

There appears to exist a considerable body of literature on coagulation starting with the theoretical work of Smoluchowski¹ and Zsigmondy² in 1917 and covering half a century³⁻⁷. In particular, the chapters of Fuchs⁵, Zebel⁶ and Hidy and Brock⁷ give valuable contemporary reviews of the subject. Although these authors are primarily concerned with the treatment of aerosol clouds suspended in the atmosphere, many of the methods, namely those in the continuum limit, can be equally well applied to collections of particulate matter suspended in a fluid medium such as liquid oxygen. This section of our report is in a large measure based on the information in these chapters.

Coagulation equation

The particle size distribution of a coagulating collection of particles as a function of the time t is usually specified by a distribution function $n(v;t)$. It is defined such that the number dN of particles per unit volume with a volume† between v and $v + dv$ is given by^{7,8}.

† In this section of the report we denote the volume of the particles by a lower case v and the velocity of the particles by a capital V .

$$dN = n(v;t) dv \quad (2.1)$$

The most general form of a coagulating equation that we were able to find is the one studied by Melzak^{8,9}.

$$\begin{aligned} \frac{\partial n(v,t)}{\partial t} = & \frac{1}{2} \int_0^v K(u, v-u) n(u;t) n(v-u;t) du - n(v,t) \int_0^v K(v,u) n(u;t) du \\ & + \int_v^\infty n(u;t) L(u,v) du - \frac{n(v;t)}{v} \int_0^v u L(v,u) du \end{aligned} \quad (2.2)$$

The function $K(u,v)$ is referred to by a number of names such as coagulation rate, coalescence kernel or coalescence rate. It is defined such that $K(u,v) n(u;t) n(v;t) du dv dt$ is the average number of particles with volumes between u and $u+du$ and v and $v+dv$ that collide in the time interval dt and which upon colliding stick to each other. Similarly, $L(u,v)$ represents a breakup function such that $n(u;t) L(u,v) du dv dt$ is the average number of particles of volume between v and $v+dv$ created from the breakup of particles of volume between u and $u+du$ during the time interval dt . Obviously $L(u,v) = 0$ if $v > u$. The meaning of the four terms in (2.2) is readily apparent. The first term represents the increase of the numbers of particles with volume v due to the coagulation of particles with volume u and $v-u$. The second term represents a decrease due to the fact that some particles with volume v coagulate with other particles. The third term represents an increase due to the breakup of particles with volumes larger than v . The fourth term represents a loss due to the fact that some particles with volume v may be split as a result of collisions. The equation (2.2) is formulated so that it satisfies conservation of volume or mass of the particles.

Although Melzak made an extensive mathematical analysis of the properties of this equation, in all applications we are aware of the breakup function $L(u,v)$ is taken to be zero. This is based on the physical observation that it is very difficult for the particles, once coagulated, to break up as a result of collisions. Hence, the equation commonly referred to as the coagulation equation reads

$$\begin{aligned} \frac{\partial n(v;t)}{\partial t} &= \frac{1}{2} \int_0^v K(u, v-u) n(u;t) n(v-u;t) du \\ &- n(v,t) \int_0^\infty K(v,u) n(u;t) du \end{aligned} \quad (2.3)$$

The theory of coagulation or agglomeration can be conceptually divided in two parts. First one needs to determine the coagulation function $K(u,v)$ of two particles of specific sizes in the medium at hand. Secondly, for a specified coagulation function one can study the evolution of the size distribution $n(v,t)$ as a function of time from a given initial distribution by solving (2.3). The coagulation equation (2.3) can be solved approximately by a variety of perturbation or computer simulation techniques. An extensive review of methods for solving the coagulation equation has been presented by Drake⁸. Due to the nonlinear character of the coagulation equation (2.3) solving the equation is a tedious process, while the solution is sensitive to the detailed nature of the coalescence function $K(u,v)$. Nevertheless, with modern computer techniques application of this equation in modelling the phenomena in the fluid density separator would appear to be a feasible task.

However, before applying the coagulation equation for the problem at hand two remarks must be made. First, the coagulation equation (2.3) commonly accepted does not incorporate any mechanism for breaking up of the coagulated particles. Hence, any theoretical analysis based on the coagulation equation cannot yield any information how to deagglomerate coagulated particles. In fact, we did not find much information how to deagglomerate coagulated particles other than by changing the chemical nature of the suspending fluid. The effects of agitation of the suspension by such methods as stirring¹⁰ or introducing acoustical waves^{11,12}, if any, may well enhance the coagulation rate. Hence, it would seem imperative that the particulates are well separated when introduced into the liquid oxygen. The coagulation equation (2.3) may then be used to investigate whether the size distributions would change significantly within the time rate of the separation process.

Secondly, the coagulation equation (2.3) used in the literature assumes that the distribution $n(v;t)$ is independent of the position of the particle in the fluid and thus is limited to suspensions that are homogeneously distributed in the fluid. Therefore, the equation as it stands can only be applied to our problem if the initial particle size distribution is homogeneous and to the extent that the coagulation rate $K(u,v)$ is independent of the position in the fluid; the latter assumption means that we neglect the spatial variation of velocity of particles of a given size. However, as we shall discuss below, starting from a truly homogeneous distribution may in fact be disadvantageous to minimize the effect of coagulation. Hence, in order to use the coagulation equation in modelling the fluid density separator it may be necessary to generalize this equation to a spatially inhomogeneous particle distribution.

Coagulation rate

We next turn our attention to the coagulation rate that determines the coalescence kernel $K(u,v)$ in the coagulation equation (2.3). The coagulation rate is determined by the probability that two particles collide and, upon colliding, will stick to each other. For this purpose one associates with each particle a sphere of influence of a certain radius R and assumes that two particles will stick together when they enter each others sphere of influence. It is possible to introduce a factor α ($0 < \alpha < 1$) accounting for the efficiency of collisions for sticking together. In fact, it is conceivable that this contact efficiency α is itself dependent upon the size of the particles; that is, one can well imagine that two particles are more likely to coalesce when one of the particles is small than when both particles are large. Introduction of such a size dependent contact efficiency would increase the complexity of the coagulation equation. However, the contact efficiency is always treated as a constant in which case a solution for $\alpha < 1$ can be readily obtained as a generalization of the usual procedure in which the contact efficiency is taken to be unity. Factors hampering the coagulation process are then taken into account by assuming a more complicated interaction between the particles such as the presence of a potential barrier. Hence, the coagulation rate is treated as proportional to the number of collisions, if properly evaluated. In the theory of coagulation the particles are usually assumed to be spherical. Nonsphericity has in general the effect of increasing the coagulation rate^{5,6}, but modelling

the fluid density separator for spherical particles would probably give a reasonable estimate of the effect.

The coagulation rate can be caused by a number of mechanisms. The first mechanism is that of thermal coagulation in which the approach of the particles, leading to contact, is effected by Brownian motion. The case of thermal coagulation is the one considered most frequently in the literature and its theoretical treatment appears to be rather well developed.^{5-8, 13-15} When the suspension contains particles of very different sizes it is known that the smaller particles disappear much more quickly than the large ones^{13,16}. The presence of electrical charges may greatly alter the rate of coagulation^{17,18} and in particular, greatly enhance, the rate of coagulation when the charges are of opposite sign.⁵

As shown in Section I, the Brownian motion of the particles is the liquid oxygen is small compared to the velocity induced by the presence of the magnetic and gravitational field. Hence, thermal coagulation does not appear an important mechanism in the operation of the fluid density separation system. However, the fact that the fine powders, even in the dry state, tended to agglomerate severely, may indicate the presence of electrical charges.

Another potential method for coagulation is known as surface coagulation. It has been observed that, by stirring the suspending fluid, coagulation is significantly enhanced when the particles come into contact with the liquid-air interface^{10,19}. As a related phenomenon, appreciable coagulation was observed when gas was bubbled through sols of ferric oxide^{20,21}. Hence the procedure of sprinkling the powder onto the surface of liquid oxygen does not appear to be recommended, since it will subject the particles to the mechanism of surface coagulation; rather they should be introduced into the bulk of the liquid.

An important mechanism for our problem, referred to as kinematic coagulation, when the motion of the particles is caused by the presence of an external field. It is usually applied to coagulation in gravitational setting^{5,6,7} and it is an obvious mechanism to be considered in the density separation process. The coagulation rate is proportional to the number of collisions, and, hence, to the velocities that the particles experience relative to each other. When all the particles move with uniform velocity the number of collisions is unaffected by the presence of the external force

and kinematic coagulation is unimportant. However, as shown in Part I, small particles in the liquid oxygen in the presence of a magnetic field exhibit a much smaller velocity than the large particles. As a consequence, there will be a tendency for a large particle to sweep out all small particles in a cylindrical column around its trajectory. Thus kinematic coagulation must be considered in the fluid density separator.

Assuming a contact efficiency $\alpha = 1$ and neglecting the effect of electrical charges the coagulation kernel for kinematic coagulation can be approximated by⁷.

$$K(u,v) = \pi (R_u + R_v)^2 V_{uv} = \left(\frac{3}{4}\right)^{2/3} \pi^{1/3} (u^{1/3} + v^{1/3})^2 V_{uv} \quad (2.4)$$

to be substituted into the coagulation equation (2.3). Here $R_u = (3u/4\pi)^{1/3}$ is the radius of a particle with volume u and V_{uv} is the relative velocity between particles with volumes u and v . A complication arises due to the fact that the relative velocity V_{uv} not only depends on the size of the particles, but also on the density of the particles. In order to avoid the introduction of an additional density variable in the coagulation equation, the actual relative velocity V_{uv} may have to be replaced with a density averaged relative velocity deduced from the analysis discussed in part I.

As mentioned earlier an excellent survey of the methods for solving the coagulation equation has been presented by Drake⁸. It would seem feasible to analyse the coagulation equation with a coagulation kernel of the type given in (2.3) using computer techniques. Such an analysis should be conducted in conjunction with computer modelling of the velocity field. Owing to the nonlinear character of the coagulation equation, such an analysis is not simple and could easily require an effort of the order of a man year. Since kinematic coagulation is the dominant mechanism, the problem has many mathematical similarities to the phenomenon at the coalescence of water droplets in clouds and fogs, which problem has been studied extensively using numerical techniques.²²

However, without solving the coagulation equation, some useful remarks can be made.

In order to minimize the coagulation we need to minimize the number of collisions between the particles. Now if the particles are initially distributed homogeneously in the liquid, we give the larger particles maximum opportunity to overtake the smaller particles. On the other hand, neglecting the effect of horizontal velocity components, the number of collisions would be small if the particles, mutually separated, are dispersed initially in a thin horizontal layer in the liquid.

In principle, coagulation can be enhanced as a result of dipoles induced in the particles by the magnetic field. However, this effect does not seem to be important at the field strength used in the fluid density separator^{5,6}.

Tentative conclusions.

1. It appears highly desirable that the particles are deagglomerated prior to insertion in the liquid oxygen. Once agglomerated, it is difficult to separate the particles again. No theoretical or experimental guidelines for deagglomerating the particles submersed in liquid oxygen could be found in the literature thus far consulted.

2. Dropping of the particles on the liquid oxygen may subject the particles to surface coagulation and, hence, enhance agglomeration of the particles.

3. The possibility that the smaller particles agglomerate as a result of electrical charges cannot be discounted.

4. It is possible to analyze numerically the evolution of the size distribution as a function of time due to kinematic coagulation in conjunction with computer modelling of the velocity field along the lines described in this report. However, this procedure requires solving a nonlinear integro-differential equation.

5. Without solving the coagulation equation the advice can be given that the number of collisions should be made as small as possible. Thus it would appear advantageous to introduce the particles well separated into a thin layer in the bulk of the liquid.

References

1. M. Smoluchowski, Z. physik. Chemie 92, 129 (1917).
2. R. Zsigmondy, Z. physik. Chemie 92, 600 (1917).
3. H. Freundlich, Kapillarchemie, Vol. II (Leipzig, 1932).
4. Coagulation and Flocculation, "Discussions Faraday Society no. 18 (1954), Part I.
5. N. A. Fuchs, The Mechanics of Aerosols" (MacMillan, New York, 1964) Ch. VII.
6. G. Zebel in "Aerosol Science," C. N. Davies, ed. (Academic Press, New York, 1966). Ch. II.
7. G. M. Hidy and J. R. Brock, "The Dynamics of Aerocolloidal Systems," (Pergamon Press, New York, 1970). Ch. 10.
8. R. L. Drake, in "Topics in Current Aerosol Research," Vol 3, G. M. Hidy and J. R. Brock, eds. (Pergamon Press, New York, 1972). Part 2. pp. 201-376.
9. Z. A. Melzak, Trans. Am. Math. Soc. 85, 547 (1957).
10. W. Heller, in "Colloidal Dispersions and Micellar Behavior," in ACS Symposium Series 9, K. L. Mittal, ed. (American Chemical Society, Washington, D. C. 1975). Ch. 3.
11. Reference 5, p. 315.
12. Reference 6, p. 52.
13. H. Muller, Kolloid- Z. 38, 1 (1926); Kolloidchem. Beihefte 26, 257 (1928).
14. S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).
15. H. Green and W. Lane, "Particulate Clouds: Dusts, Smokes and Mist," 2nd ed. (Van Nostrand, Princeton, N. J. 1964).
16. J. Th. G. Overbeek, in "Colloid Science," Vol. I., H. R. Kruyt, ed. (Elsevier, Amsterdam, 1952), Ch. 7.
17. T. Gillespie, Proc. Roy. Soc. London A216, 569 (1953).
18. S. L. Loo in "Topics in Current Aerosol Research," Vol. 2, G. M. Hidy and J. R. Brock, eds. (Pergamon Press, New York, 1971), pp. 61-149.
19. H. Freundlich and R. Von Recklinghausen, Z. physik. Chem. A157, 325 (1931).
20. H. Stark, J. Am. Chem. Soc. 52, 2730 (1930).
21. W. Heller, Comp. Rend. 198, 1776 (1934).
22. E. X. Berry, J. Atm. Sciences 24, 688 (1967).

Acknowledgment

The authors are indebted to Dr. D. T. Gillespie of the Naval Weapons Center for some valuable comments.

